PB82-227489

Chemical Composition of Produced Water at Some Offshore Oil Platforms

Rockwell International
Newbury Park, CA

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Mar 82

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EPA-600/2-82-034
March 1982

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CHEMICAL COMPOSITION OF PRODUCED WATER AT SOME OFFSHORE OIL PLATFORMS

by

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Contract No. 68-03-2648

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-82-034	ORD Report	PB82 227489

4. TITLE AND SUBTITLE	5. REPORT DATE
Chemical Composition of Produced Water at Some Offshore Oil Platforms	March 1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Ihor Lysyj	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Rockwell International 2421 West Hillcrest Drive Newbury Park, California 91320	1NE826
	11. CONTRACT/GRANT NO.
	68-03-2648
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Municipal Environmental Research Laboratory - Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	Final Report, 1/80 to 11/80
	14. SPONSORING AGENCY CODE
	EPA/600/14

15. SUPPLEMENTARY NOTES

John S. Farlow, Project Officer (201-321-6631)

16. ABSTRACT

The effectiveness of produced water treatment was briefly studied in offshore oil and gas extraction operations in Cook Inlet, Alaska, and the Gulf of Mexico. Three offshore oil extraction facilities were examined in the Cook Inlet production field, and seven platforms were studied in the Gulf of Mexico. Overall treatment effectiveness, as well as effectiveness of individual process units, was determined in the Cook Inlet study. Quality of the final effluent was characterized in the Gulf of Mexico study.

The state-of-the-art treatment technology was generally effective in reducing free oil content (suspended organics) of produced water. The treatment was less effective in reducing aromatic hydrocarbon content in produced water (average reduction in concentration was of the order of 30% to 50%). Benzene, toluene, and xylenes/ethylbenzene (BTX) were found at all stages of the processes and in all final effluents. The average BTX concentration in treated effluents from Cook Inlet operations was 9 mg/L. In Gulf of Mexico treated effluents, the BTX content averaged 2 mg/L. High levels of dissolved nonvolatile organic matter (ranging from 60 to 600 mg C/L) were found in all treated effluents. Four organic priority pollutants (benzene, toluene, ethylbenzene, and phenol) and two inorganic priority pollutants (chromium and lead) were found in all treated effluents analyzed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Oil Recovery Water Treatment Water Pollution Oils Aromatic Hydrocarbons	Oil and Gas Extraction Water Treatment Effectiveness Dissolved Organics Offshore Platforms Cook Inlet (Alaska) Gulf of Mexico	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	UNCLASSIFIED	57
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report presents the results of sampling and analysis of produced waters, as well as final treated effluent, in a number of selected offshore oil and gas extraction operations. Limited information on priority pollutant content in treated effluent is also reported. The results will be of interest to all those interested in the treatment of oil-contaminated water.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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ABSTRACT

The effectiveness of produced water treatment was studied in a number of selected offshore oil and gas extraction operations in Cook Inlet, Alaska, and the Gulf of Mexico. Three offshore oil extraction facilities were examined in the Cook Inlet production field, and seven platforms were studied in the Gulf of Mexico. Overall treatment effectiveness, as well as effectiveness of individual process units, was determined in the Cook Inlet study. Quality of the final effluent was characterized in the Gulf of Mexico study.

The chemical composition of process streams and final effluents were characterized in terms of total organic material balance. Determinations were made for suspended organic matter (free oil), dissolved nonvolatile organic matter, and volatile hydrocarbons.

The state-of-the-art treatment technology was generally found to be effective in reducing the free oil content (suspended organics) of produced water, but it was less effective in reducing the aromatic hydrocarbon content. Average reduction in concentration of aromatic hydrocarbons was on the order of 30% to 50%. Benzene, toluene, and xylenes/ethylbenzene (BTX) were found at all stages of the processes and in all final effluents. The average BTX concentration in treated effluents from Cook Inlet operations was 9 mg/L. In Gulf of Mexico treated effluents, the BTX content averaged 2 mg/L.

High levels of dissolved nonvolatile organic matter (ranging from 60 to 600 mg C/L) were found in all treated effluents. Generally, the concentration of this fraction increased rather than decreased as a result of treatment. This increase may be due to addition of chemicals during the treatment and oxidation of petroleum matter leading to formation of water-soluble oxygenated organic compounds. Four organic priority pollutants (benzene, toluene, ethylbenzene, and phenol) and two inorganic priority pollutants (chromium and lead) were found in all treated effluents analyzed. Intermittently present were naphthalene, cadmium, zinc, nickel, silver, copper, and beryllium.

This report was submitted in partial fulfillment of Contract No. 68-03-2648 by Rockwell International under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period January 1980 to November 1980, and work was completed as of January 1981.

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ACKNOWLEDGMENTS

We wish to thank Mr. Bill Lamoreaux, U.S. Environmental Protection Agency (EPA), Alaska Operations Office, Anchorage, Alaska, for his assistance in carrying out field sampling operations in Cook Inlet; Commissioner Ernest W. Mueller, State of Alaska, Department of Environmental Conservation, Juneau, Alaska; and Mr. Doug Lockwood, Alaska Department of Environmental Conservation, Valdez, Alaska, for use of their facilities and essential assistance.

Samples of produced water in the Gulf of Mexico were collected by Texas Instruments Company personnel. Priority pollutant analysis was performed under contract to the EPA by Analytical Research Laboratories, Monrovia, California; Battelle, Columbus, Ohio; Monsanto Research Corp., Dayton, Ohio; and ERCO, Cambridge, Massachusetts.

The Rockwell International team, composed of Ihor Lysyj, George Perkins, David Janka, and Kathy Doering, conducted the field study in Cook Inlet.

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SECTION 1

INTRODUCTION

A detailed study of ballast water treatment effectiveness was conducted in Port Valdez, Alaska, in 1978-1980 (1). Port Valdez is a terminal of the TransAlaska Pipeline, where oil from Prudhoe Bay is transferred into oil tankers. Before accepting the oil, tankers must discharge large amounts of ballast water into the rather sheltered waters of the small (5 km wide by 18 km long) subarctic estuary. The volume of ballast water discharged is rather large; an average of 50,000 m^3 is discharged daily. This is as much as one-half of the total discharge from all oil-producing platforms in the offshore coastal shelf of the Gulf of Mexico (97,000 m^3 per day during 6 months of 1979). Because of such large discharges of contaminated water into the sheltered coastal fjord, this problem is of major concern to the State of Alaska.

In order to characterize treatment plant effectiveness and determine the quality of the final effluent, special analytical techniques and procedures were developed (1, 5). A technique based on organic material balance provided a comprehensive picture of the chemistry of the ballast water in the treatment process and receiving environment.

One of the principal findings of this EPA-sponsored research on ballast water treatment (1) was the fact that benzene, toluene, and xylenes (BTX) constituted almost half of the petroleum-derived material in the treated effluent discharged to the environment. Approximately 7 to 9 tons of BTX are discharged into receiving waters of Port Valdez by the treatment plant each month. Whether this resulted from the nature of the treatment (gravity separation, gas flotation and impoundment) or from contact of the saline water and the petroleum either in the reservoir or in tanker cargo tanks was not known.

The purpose of the more limited study reported here was threefold:

a. To determine how applicable organic material balance procedures are to analysis of offshore oil and gas produced water

b. To obtain some data on the range of variability of treated offshore oil and gas produced water in terms both of the components of the total organic material balance and of the various EPA-designated priority pollutants

c. To collect limited information on the effectiveness of the treatment of produced water in offshore oilfields of Alaska

This information is of interest in planning the emphasis for future research.

By a fortunate coincidence, a detailed study of the oil variability in treated brine was just beginning the second round of field sampling on seven Louisiana offshore oil and gas production platforms. By obtaining additional samples of the treated effluent (which could be subjected to the same protocol carried out with the same personnel and equipment at Valdez, Alaska), it might be possible to shed some light on one corner of the question raised by the ballast water treatment study. At the same time, the field method developed for the ballast water plant itself could be checked against the results of the platform treated brine study.

As a further bonus, an opportunity to collect samples for priority pollutant analysis would provide still another type of check (since both benzene and toluene are priority pollutants).

It also turned out to be possible to obtain effluent samples from three Cook Inlet, Alaska, production operations, providing yet another comparison of treated brines from different oil fields.

It should be noted at the outset that, at most, only a few samples were collected at each location during this brief study; this study is not nearly as extensive or detailed as either the ballast water treatment plant study (1) or the Louisiana platform brine study (2).

This study had two major field sampling efforts, each carried out in two different locations:

Effort 1 - Collect samples for determining the organic material balance at one or more points at each facility, and

Effort 2 - Collect samples for priority pollutant analysis at one or more locations at each facility:

Location 1 - Louisiana offshore oil production area, and
Location 2 - Alaska's Cook Inlet oil production area.

The organic material balance samples from Cook Inlet were taken to Valdez, Alaska, for analysis. Hydrochloric acid was added as a preservative (to pH 2), and the total time elapsed from drawing the sample to arrival at the laboratory was in the order of 36 hours. The samples from the Gulf of Mexico were shipped to Rockwell's base at Newbury Park, California. There, HCl (to pH 2) was added as a preservative, and the samples were shipped on to Valdez, Alaska, for analysis. The total time from drawing the sample to arrival at the analytical laboratory was approximately 7 days. Part of this time the samples from the Gulf Coast were not preserved. The samples for material balance were maintained at ambient temperature, while priority pollutant samples were maintained at 4°C.

The priority pollutant samples from Cook Inlet became delayed in transit for almost a week and arrived at the EPA Effluent Guidelines Division contract

laboratories too long a time after being drawn to be worth the effort of analyzing.

The samples from the Gulf of Mexico (six effluent samples and three gas flotation unit influent samples, one of which of the latter had obviously been contaminated) were also shipped to EPA Effluent Guidelines Division contract laboratories, and were analyzed.

Sampling operations were carried out by Rockwell or its subcontractors on the following schedule:

Location	Organic Material Balance Sample Date	Priority Pollutants Sample Date
Gulf of Mexico		
BM 2C	7 March	13 March
SS 107	10 March	(no sample)
ST 131	21 March	19 March
SS 198G	24 March	21 March
EI 18CF	2 April	8 April
BDC CF5	4 April	8 April
SM 130B	(no sample)	17 April
Cook Inlet		
Trading Bay (onshore)	23 January[a]	(no sample)
Dillon (offshore)	6 August[b]	6 August[d]
Kenai (onshore)	7 August[c]	7 August[d]

a. Three sample sets taken at discrete time intervals.

b. One set of triplicate samples taken between 0900 and 1200.

c. One set of duplicate samples taken between 0900 and 1200.

d. Samples reached laboratory after time limit expired; not analyzed.

SECTION 2

CONCLUSIONS

As a result of brief studies dealing with the operation of three offshore oil and gas extraction facilities in Cook Inlet, Alaska, and examination of the effluent from seven offshore oil-producing platforms in the Gulf of Mexico, the following conclusions can be drawn:

1. The treatment technology is (generally) based on gravity separation and gas or air flotation. On the average, reductions in excess of 90% of the free oil in the produced water are realized.

2. The suspended organic matter (or free oil) in the treated effluent in the Cook Inlet production field ranged between 5 and 36 mg C/L.* The average free oil concentration in the treated effluent was 18 mg C/L.

3. Suspended organic matter (or free oil) in the treated effluent in the Gulf of Mexico ranged between 9 and 46 mg C/L. The average free oil concentration in the treated effluent was 26 mg C/L.

4. Volatile aromatic hydrocarbons composed largely of benzene, toluene, and xylenes/ethylbenzene were found in all process streams and in all treated effluents tested. Total aromatic hydrocarbon content in the treated effluent was found to average 9 mg/L from Cook Inlet operations and approximately 2 mg/L in the Gulf of Mexico effluent.

5. Treatment processes were far less effective in the removal of volatile aromatic hydrocarbons from the process stream. Removal rates were on the order of 30% to 50%.

6. High concentrations of dissolved organic matter were found in all treated effluents. Dissolved nonvolatile organic content in the treated effluents from the Cook Inlet operation ranged between 141 and 423 mg C/L, averaging 276 mg C/L. Dissolved nonvolatile organic content in treated effluents from the Gulf of Mexico operations ranged between 57 and 624 mg C/L, averaging 376 mg C/L.

7. Up to 90% of all organic matter present in treated discharges of produced water is made up of dissolved nonvolatile organics. Neither the source nor the nature of the dissolved nonvolatile organic matter present in produced water streams is known at this time.

---

* 1 mg C/L corresponds to approximately 1.16 mg/L of the oil.

8. Four organic priority pollutants were found consistently in discharges from offshore oil and gas extraction operations: benzene, toluene, ethylbenzene, and phenol. One was found intermittently: naphthalene.

9. Two metal priority pollutants were found in all treated produced water effluents: chromium and lead. Intermittently present were zinc, beryllium, cadmium, copper, silver, and nickel.

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SECTION 3

RECOMMENDATIONS

1. The source and nature of dissolved nonvolatile organics should be established. Processes leading to the formation of such organic compounds during treatment should be delineated.

2. Methods for reducing the concentration of principal organic priority pollutants present in treated produced water (benzene, toluene, and ethylbenzene and phenol) should be developed.

3. Methods for reducing the concentration of metal priority pollutants should be considered.

4. Evaluation of the relative toxicity of dissolved nonvolatiles should be determined.

5. An evaluation should be undertaken of alternative treatment technologies to remove some of these nonvolatile compounds contingent on concentration and their toxicity.

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SECTION 4

METHODS

Two different types of analytical methodologies were used in this study. One protocol was designed to establish the organic material balance in the process stream. This protocol addressed quantitatively the principal fractions of organic matter present in produced water: suspended organic matter, dissolved nonvolatile organic matter, and volatile hydrocarbons. The second protocol was designed to determine priority pollutants quantitatively, including: purgeables, acid-neutral, base-neutral, pesticides, and metals. EPA-approved methods of analysis for priority pollutants were used.

A description of the methods used, as well as sampling procedures and quality control, follows.

SAMPLING PROCEDURES

Two basic types of sampling procedures were used: one for material balance determination, and the second for priority pollutants. Samples for material balance determinations were collected in 1-liter glass bottles, the caps of which were lined with aluminum foil. Samples were preserved by acidification with hydrochloric acid to pH 2.

Samples for priority pollutant analysis were collected according to the EPA sampling procedure; purgeables were collected in 40-ml vials equipped with Teflon-lined septums. Samples for acid-neutral, base-neutral, and pesticides analysis were collected in glass containers, the caps of which were lined with Teflon. Samples for metal analysis were collected in plastic containers.

QUALITY CONTROL

The objective of quality control in analytical chemical work is to assure that generated data correctly reflect parameters of properly defined and accurately measured phenomena. This is done by eliminating false-positive and false-negative bias from the data and providing statistical validity in the accuracy and reproducibility of the reported data. The principal elements of a good quality control protocol are instrumental and procedural blank determination, recovery data, multiple analysis of samples, daily multipoint calibration of instrumentation, statistical documentation of the accuracy and reproducibility of the methods used, and well-maintained documentation of all laboratory and sampling operations. A discussion of the key elements of quality control protocol utilized during the field and laboratory operations follows.

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Contamination Check

To assure the absence of contributions from the sample matrix and solvents, determinations of blank values were carried out daily on the gas chromatograph and TOC analyzer. The values for blanks were compensated for in the calculation of results.

Recovery

Recovery studies were conducted for all chemical compounds that required separation from the water matrix as a part of the analytical procedure. Model chemical compounds were introduced in known quantities in 850-ml water samples and then analyzed in a manner identical to real samples. Recovery values were established for benzene, toluene, and xylenes.

Replicates

All analyses were performed in triplicate, within a specified reproducibility range.

Calibration

Multipoint calibrations for n-hexane (model for aliphatic hydrocarbons), benzene, toluene, and xylenes were performed daily and new calibration graphs were prepared each day and used only during that day of operation. Multipoint calibration for TOC analysis was also performed daily using a potassium acid phthalate standard solution. Comparisons of daily calibration curves were made to detect any differences and/or drift in instrumental responses and/or changes in the composition of standard solutions.

Accuracy and Reproducibility

Accuracy and reproducibility of all procedures used were established either from the literature (for standard methods) or determined experimentally for research procedures developed under this program.

OILY WASTEWATER ANALYTICAL PROTOCOL

In order to develop information on the effectiveness of oil removal and to characterize the chemical redistribution taking place in the process, it was necessary to measure the concentrations of each organic fraction and to characterize chemically the principal compounds present.

To do so, an analytical protocol (Figure 1) (1, 5) was devised that included:

1. Determination and chemical characterization of volatile organic fraction
2. Determination of dissolved nonvolatile fraction
3. Determination of suspended organic matter

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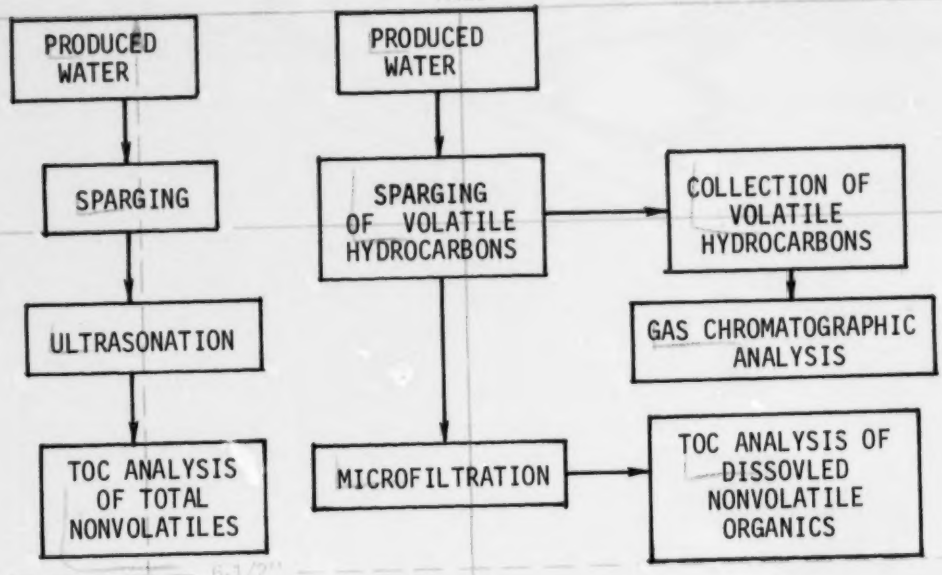

Figure 1. Oily wastewater analytical protocol.

In order to define overall organic concentration in the process stream, the Total Organic Load (TOL) was established. This corresponds to the sum of the volatile organics, dissolved nonvolatile organic matter, and suspended organic materials. The TOL value is expressed in mg C/L. The value of volatile hydrocarbons (which were determined as mg hydrocarbons/liter) was converted to mg C/L expression. Proportions of carbon to hydrogen in the principal hydrocarbons found (benzene, toluene, and xylenes) were used to calculate mg C/L values. Values for dissolved nonvolatile organics and for suspended organic matter were determined as mg C/L, and added to the converted values of volatile hydrocarbons. All TOL values reported here were so calculated.

Analysis of Volatile Fraction

The volatile fraction of the process stream was composed largely of lower aromatic hydrocarbons (benzene, toluene, xylenes, and ethylbenzene). Some lower aliphatic hydrocarbons were present in the effluent from the gravity separator. Gas chromatographic procedure was used for analysis of this fraction.

A water sample (850 to 1000 ml) was sparged by the nitrogen gas and volatile hydrocarbons were adsorbed in an activated charcoal cartridge. Adsorbed hydrocarbons were then dissolved into 1 ml of carbon disulfide, providing for an 850- to 1000-fold concentration of volatile organic matter. A sample of this concentrate was injected into a gas chromatograph, separated into discrete fractions, and quantified using a hydrogen flame ionization detector.

Using this method and a Gow-Mac gas chromatograph, the detection limit for individual hydrocarbons was estimated at 0.1 microgram/liter, or 0.1 ppb (parts per billion). The identities of eluting peaks were established using

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computerized gas chromatograph - mass spectrometer (GC-MS). The quantification was performed using either peak or area measurements on gas chromatograms.

Analysis for Dissolved Nonvolatile Organic Compounds

The suspended oil was separated from the dissolved organic matter by Millipore filtration using a 0.45-micron HA filter. The acidified and sparged filtrate was used for determination of total organic carbon (TOC) using Standard Method 510 (6).

Determination of Suspended Organic Matter

A water sample was acidified, sparged with nitrogen, and ultrasonated using a Braun-Sonic Model 1510 probe at 300 watts power. The emulsified sample was injected into the TOC analyzer and total organic carbon was determined using Standard Method 510 (6). The suspended organic matter was determined as a difference between the concentration of total nonvolatiles and dissolved organics. This fraction contained primarily aliphatic hydrocarbons of petroleum origin, and was not further chemically characterized.

PRIORITY POLLUTANT ANALYSIS

Priority pollutant analysis was carried out according to EPA-specified methods (40CFR136) (4) by other commercial laboratories under contract to the EPA Effluent Guidelines Division.

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SECTION 5

FIELD STUDIES

Evaluation of the effectiveness of state-of-the-art technology in the treatment of offshore produced water (brine) was carried out in Cook Inlet, Alaska, and offshore in the Gulf of Mexico.

Three production facilities were examined in Cook Inlet. Two of these treated offshore produced water onshore and one treated offshore produced water on the platform itself. One onshore treatment facility treated produced water by gravity separation (skim tanks), gas flotation (Wemco), and impounding. The second onshore treatment facility treated produced water by gravity separation and dissolved air flotation. The offshore treatment facility was a single-stage separation by gravity.

Reduction of organic load in the process streams was studied by analysis for suspended organic matter (free oil), dissolved nonvolatile organic composition, and volatile organic compounds at various points of the treatment processes.

Seven offshore oil and gas production facilities were examined in the Gulf of Mexico. All of those treated brine on-site. Primary treatment was by gravity, and secondary treatment was by gas flotation. Treated effluents from oil and gas producing platforms were examined in terms of organic material balance, including suspended organic matter, dissolved nonvolatile organics, and volatile hydrocarbon. Additionally, priority pollutants analysis was performed for purgeables, acid-neutral, base-neutral, pesticides, and metals.

COOK INLET, ALASKA

Evaluation of the effectiveness of offshore produced water treatment in Cook Inlet was conducted in 1980. Three different treatment operations were selected to reflect various degrees of technical sophistication in the treatment.

In one case, offshore produced water (brine) was treated in a modern, well-operated onshore treatment plant. The second case also involved onshore treatment of offshore produced water in a plant of older design. The principal difference between the two plants was use of dissolved gas flotation in the newer facility and dissolved air flotation in the older facility. The newer facility (Trading Bay, Alaska) was also equipped with two holding ponds, while the older (Kenai, Alaska) was not.

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In the third case, produced water was treated in a simple, one-step gravity separation operation on the offshore platform.

It is believed that these selected treatment operations are representative of principal practices in Cook Inlet.

Trading Bay Production Facility

Evaluation of treatment effectiveness at the Trading Bay production facility was conducted on January 23, 1980. This facility is located on the northwestern shore of Cook Inlet, approximately 60 air miles southwest of Anchorage. Four offshore platforms supply gross fluid for onshore processing. The fluid is piped into a battery of heater-treaters where oil is separated from the water in heated chambers and then transferred into two batteries of storage tanks. One battery consists of six 10,000-barrel (1590 m^3) tanks, the other is of two 45,000-barrel (7155 m^3) tanks. Natural gas is also generated and processed at this facility.

The production facility processes 131,000 barrels (20,829 m^3) of gross fluid per day and generates 67,000 barrels (10,653 m^3) of oil and 62,000 barrels (9858 m^3) of produced water (brine). Natural gas is generated at a rate of 28,000 MCFPD (792,880 standard m^3/d). Storage capability of petroleum products includes 150,000 barrels (23,850 m^3) of oil and 10,000 barrels (1590 m^3) of liquid petroleum gas (LPG).

Treatment Plant--

This modern plant for treatment of produced water (Figure 2) consists of three gravity separators of 10,000-barrel (1590 m^3) capacity, two gas flotation units, and two water retention ponds of 50,000-barrel (7950 m^3) capacity. Treated ballast water is discharged offshore into Cook Inlet receiving waters. The quality of the process water is monitored routinely by the oil company personnel at various process points, and at the final discharge point.

The treatment plant at the Trading Bay production facility appeared to be overdesigned for present loading in anticipation of future increases in volume of produced water, and on the day of sampling it operated at approximately 50% of its capacity.

Sampling and Analysis--

In order to characterize effectiveness of the three principal treatment units (gravity separators, gas flotators, and retention ponds), four sampling stations were selected (Figure 2). The effluent from the heater-treaters, which separate oil from water, represents input into the produced water treatment plant. A sample of this effluent was collected from an existing sampling outlet, Station 1. Station 2 was an existing sample tap used by operating personnel for routine sampling of process water from a line exiting the gravity separator. The effluent from the gravity separators is directed into one of two gas flotation treatment units. Unit No. 2 was in operation on the day of sampling and water samples were taken from a tap used for routine sampling by the plant operating personnel. This sampling point was designated Station 3. Process water from the gas flotator enters one of two 50,000-barrel (7950 m^3) retention ponds, where it is kept under quiescent conditions prior to discharge

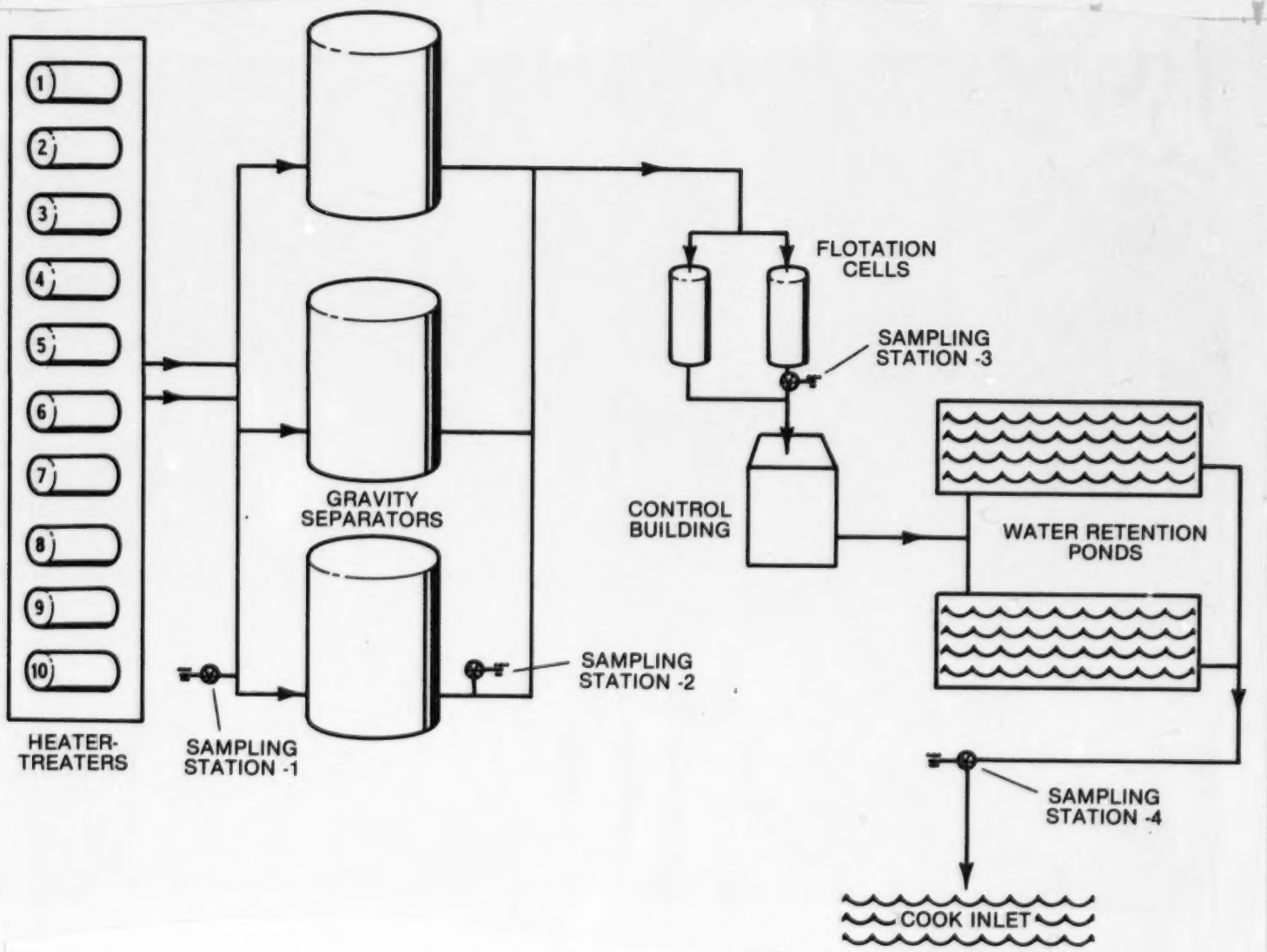

Figure 2. Trading Bay facility.

into receiving waters of Cook Inlet. Water retention pond No. 2 was in operation on the day of sampling. Effluent from the retention pond was collected in a sampling well from a sampling tap used for routine monitoring of treated effluent. This sampling point was designated Station 4.

Three sets of samples were collected over a 5-hour period to provide a daily average of typical chemical composition of produced water. Sampling during each time sequence was initiated at Station 4 (final, treated effluent) and proceeded upstream to Station 1 (effluent from heater-treaters).

Results--

Station 1, Heater-Treater Effluent. Three sets of water samples were collected at this station at 1310, 1359, and 1530 on January 23, 1980. The results of oily wastewater protocol analysis, which represent material balance for all organic matter present, are reported in Table 1. The average total organic load of the heater-treater effluent was 454 mg C/L with a standard deviation of 137 mg C/L, or 30% fluctuation. Suspended organic matter, composed primarily of free oil, was found to be 148 mg C/L with a standard deviation of 143 mg C/L. The wide fluctuation of free oil (97%) in the effluent from the heater-treaters reflected nonhomogeniety of the stream at this point in the processing.

Dissolved nonvolatile organic matter was present at a concentratidon level of 293 mg C/L, with a standard deviation of 16 mg C/L, or a fluctuation of approximately 6%. The concentration level of volatile hydrocarbons was found to be 13 mg C/L with a standard deviation of 5 mg C/L, or a fluctuation of 38%. Volatile hydrocarbons were composed of 5.0 mg C/L aliphatic hydrocarbons (38%) and 8.0 mg C/L of aromatic hydrocarbons (62%). Aromatic hydrocarbons were composed largely of benzene, toluene, xylenes/ ethylbenzene in the following ratio: 4.7:2.4:1.0.

Data reported in Table 1 reveals that the effluent from the heater-treaters was composed of 32.6% free oil, 64.5% dissolved nonvolatile organic matter, and 2.9% volatile hydrocarbons.

Station 2, Gravity Separator Effluent. Three sets of water samples were collected at this station at 1141, 1354, and 1546 on January 23, 1980. The results of protocol analysis, which represent material balance for all organic matter present, are reported in Table 2. The average organic load of gravity separator effluent was 458 mg C/L with a standard deviation of 30 mg C/L, or a fluctuation of approximately 7%, a value considerably lower than that observed in the effluent from the heater-treaters.

Aging under quiescent conditions and the averaging effect of a large-volume water body in the settling tank reduced free oil content and contributed to a greater degree of reproducibility from sample to sample. The average concentration of suspended organic matter (free oil) was found to be 38 mg C/L with a standard deviation of 16 mg C/L, or a fluctuation of approximately 42%. The drop in free oil concentration was approximately 75% as a result of gravity separator treatment, and reproducibility was considerably better at Station 2 than at Station 1.

TABLE 1. STATION 1, ORGANIC COMPOSITION OF HEATER-TREATER EFFLUENT, TRADING BAY FACILITY, JANUARY 23, 1980 (in mg C/L)

Time of Sampling	1310	1359	1550			
Water Temperature, °C	40	37.2	40			
				Average	Standard Deviation	Percent
Total Organic Load	362	389	612	454	137	
Suspended Petroleum	41	92	311	148	143	32.6
Dissolved Nonvolatile Organic Matter	312	286	282	293	16	64.5
Volatile Hydrocarbons	9.0	10.4	19.3	13.0	5	2.9
Aliphatic Hydrocarbons	3.2	3.9	8.0	5.0	2.6	1.1
Aromatic Hydorcarbons	5.8	6.5	11.3	7.9	3.0	1.7
Benzene	3.5	3.9	5.5	4.3	1.0	
Toluene	1.8	2.0	2.8	2.2	0.5	
Xylenes	0.5	0.6	1.5	0.9	0.5	
Other	0	0	1.5	0.5	0.9	

TABLE 2. STATION 2, ORGANIC COMPOSITION OF GRAVITY SEPARATOR EFFLUENT, TRADING BAY FACILITY, JANUARY 23, 1980 (in mg C/L)

Time of Sampling	1141	1354	1546			
Stream Temperature, °C	39.4	39.4	37.8			
				Average	Standard Deviation	Percent
Total Organic Load	423	476	475	458	30	
Suspended Petroleum	23	55	35	38	16	8.3
Dissolved Nonvolatile Organic Matter	389	409	429	409	20	89.3
Volatile Hydrocarbons	10.7	12.2	10.8	11.3	0.9	2.4
Aliphatic Hydrocarbons	2.6	4.3	3.9	3.6	0.9	0.8
Aromatic Hydrocarbons	8.1	7.9	6.9	7.7	0.6	1.6
Benzene	4.9	4.5	3.9	4.5	0.5	
Toluene	2.5	2.3	2.0	2.3	0.3	
Xylenes	0.7	1.1	1.0	0.9	0.2	

Dissolved nonvolatile organic matter was present in a concentration of 409 mg C/L, with a standard deviation of 16 mg C/L, or approximately 4% fluctuation. Analysis of samples from this station indicated a 28% increase, rather than a decrease, in concentration of dissolved organic fraction. Reasons for this increase are unknown at this time (but might be due to sampling a different oil parcel, addition of chemicals for treatment, and chemical changes in the character of organic matter as a result of processing of gross fluid). The concentration level of volatile hydrocarbons was found to be 11.3 mg C/L with a standard deviation of 0.9 mg C/L, or a fluctuation of about 8%. Reduction in concentration of this fraction was rather small (approximately 14%). Volatile fraction was comprised of 3.6 mg C/L (31%) aliphatic hydrocarbons and 7.7 mg C/L (69%) aromatic hydrocarbons. Aromtic hydrocarbons were composed largely of benzene, toluene, and xylenes/ethylbenzene. The ratio of each was very similar to ratios observed in samples from Station 1, i.e., 5.0:2.6:1.

Data reported in Table 2 reveals that the effluent from the gravity separator was composed of 8.3% free oil, 89.3% dissolved nonvolatile organic matter, and 2.4% volatile hydrocarbons. When compared with effluent from the heater-treaters, a proportional decrease in free oil and an increase in dissolved nonvolatile fraction is apparent.

Station 3, Gas Flotation Effluent. Three sets of water samples were collected at this station at 1090, 1351, and 1543 on January 23, 1980. The results of oily wastewater protocol analysis, which represent material balance for all organic matter present in the stream, are reported in Table 3. The average total organic load of the gas flotation effluent was 436 mg C/L with a standard deviation of 8 (a fluctuation of only 2%). Suspended organic matter, comprised primarily of free oil, was found to be 33 mg C/L, with a standard deviation of 21 mg C/L (a fluctuation of 64%). Dissolved nonvolatile organics were present at a concentration level of 394 mg C/L, with a standard deviation of 28 mg C/L (approximately 7% fluctuation). Concentration of volatile hydrocarbons was found to be 8.6 mg C/L with a standard deviation of 0.8 (9% fluctuation). The volatile fraction was composed of 2 mg C/L aliphatic hydrocarbons (23%) and 6.6 mg C/L aromatic hydrocarbons (77%). The aromatic hydrocarbons were composed essentially of benzene, toluene, and xylenes/ethylbenzene, which were present in a 4.1:2.2:1 ratio. This ratio appears to be similar to samples from two upstream stations.

Data reported in Table 3 reveals that dissolved nonvolatile organics constitute the bulk of organic load (90.4%) at this point of wastewater processing. Free oil accounted for only 7.6% of the total organic load and volatile hydrocarbons contributed only 2%.

Station 4 - Final Effluent. The results of oily wastewater protocol analysis, which represent material balance for all organic matter present in the samples, are reported in Table 4. The average total organic load of the final treated effluent was 435 mg C/L, with a standard deviation of 14 mg C/L (a fluctuation of only 3%). Suspended organic level was low, with an average equal to 5.3 mg C/L and a standard deviation of 9 mg C/L. Dissolved organic matter constituted the bulk of organic matter in the final discharge, with a concentration of 423 mg C/L (standard deviation of 10 mg C/L). It constituted

TABLE 3. STATION 3, ORGANIC COMPOSITION OF GAS FLOTATION EFFLUENT, TRADING BAY FACILITY, JANUARY 23, 1980 (in mg C/L)

Time of Sampling	1090	1351	1543			
Water Temperature, °C	38.3	39.4	38.9			
				Average	Standard Deviation	Percent
Total Organic Load	427	439	442	436	8	
Suspended Petroleum	58	18	24	33	21	7.6
Dissolved Nonvolatile Organic Matter	360	412	410	394	29	90.4
Volatile Hydrocarbons	9.1	8.8	7.6	8.6	0.9	2.0
Aliphatic Hydrocarbons	2.2	2.0	1.8	2.0	0.2	0.5
Aromatic Hydrocarbons	6.9	6.8	5.8	6.6	0.6	1.5
Benzene	3.8	3.8	3.4	3.8	0.3	
Toluene	2.1	2.1	1.7	2.0	0.3	
Xylenes	1.0	0.9	0.7	0.8	0.2	

TABLE 4. STATION 4, ORGANIC COMPOSITION OF FINAL EFFLUENT, TRADING BAY FACILITY, JANUARY 23, 1980 (in mg C/L)

Time of Sampling	1015	1336	1538			
Water Temperature, °C	29.4	28.3	29.4			
				Average	Standard Deviation	Percent
Total Organic Load	442	446	419	435	14	
Suspended Petroleum	0	16	0	5.3	9	1.2
Dissolved Nonvolatile Organic Matter	435	422	412	423	11	97.2
Volatile Hydrocarbons	6.5	7.4	6.6	6.9	0.5	1.6
Aliphatic Hydrocarbons	1.1	1.7	1.2	1.3	0.4	0.3
Aromatic Hydrocarbons	5.4	5.7	5.4	5.6	0.2	1.3
Benzene	3.4	3.6	3.0	3.4	0.3	
Toluene	1.5	1.6	1.7	1.6	0.1	
Xylenes	0.5	0.5	0.7	0.6	0.1	

97.2% of all organic matter found in the discharge. Volatile hydrocarbons were present at a concentration level of 6.5 mg C/L with a standard deviation of 0.4 mg C/L (a fluctuation of approximately 6%). Volatile hydrocarbons were composed of 1.1 mg C/L aliphatic hydrocarbons (20%) and 5.4 mg C/L aromatic hydrocarbons (80%). Aromatic hydrocarbons were composed of benzene, toluene, and xylenes/ethylbenzene in a ratio of 6.8:3.4:1.

Data reported in Table 4 reveals that the final effluent was composed largely of dissolved nonvolatile organic matter (97.2%), with a very low level of free oil (5.3 mg C/L). Toxicologically important aromatic hydrocarbons were present in significant amounts.

Discussion--

The compositional data for all four sampling stations is summarized in Table 5 as mean values of measured parameters and the standard deviation. Significant fluctuation in suspended organic matter content, as indicated by the large standard deviation values, were observed. Fluctuations in the output from the heater-treater unit and nonhomogeneity of oil-water mixtures are reasons for the wide fluctuation in such compositions.

Dissolved nonvolatile organic content, however, fluctuated very little from sample to sample and from sampling time to sampling time. Volatile hydrocarbon content fluctuated significantly in the effluent from the heater treatment, but was more stable downstream from the gravity separators.

The effectiveness of the treatment of produced water is reflected in stepwise reduction of various organic fractions, as depicted in Table 6 and Figure 3. Analysis of the reported data indicates that the treatment process is effective in reducing suspended oil and volatile aliphatic hydrocarbon concentrations. A 97% reduction in suspended organic matter resulted in an effluent containing 5 mg C/L of suspended organics. The concentration of volatile aliphatic hydrocarbons was reduced approximately 75%.

The process, however, was less effective in reducing volatile aromatic hydrocarbons. A reduction of only 30% was realized, and treated effluent contained, on average, 6 mg C/L of volatile aromatic hydrocarbons.

Very high concentrations of dissolved nonvolatile organic matter were observed at all stages of the treatment process. As a matter of fact, dissolved organic content of the final effluent was significantly higher than that of untreated effluent from the heater-treater. The increase in concentration of dissolved, nonvolatile organic matter, in all cases, took place in initial stages of treatment of produced water (between heater-treaters and gravity separators). Such an increase might be due, in part, to addition of organic chemicals used as part of the treatment. Oxidation of petroleum composition might be an additional factor in the formation of water-soluble organic matter. When essentially anaerobic produced waters are exposed to an oxygen environment at relatively high temperatures (above 100°F), autocatalytic processes might lead to oxidation of some components of organic matter present in produced water, resulting in formation of water-soluble oxygenated organic compounds.

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TABLE 5. SUMMARY OF ORGANIC COMPOSITION OF THE PROCESS STREAM, TRADING BAY FACILITY (means and standard deviations reported in mg C/L)

Component	Sampling Stations 1 Heater-Treater Effluent	2 Gravity Separator Effluent	3 Gas Flotation Effluent	4 Retention Pond (Final) Effluent
Suspended Organic Matter	148 (±143)	38 (±16)	33 (±21)	5.3 (±9)
Volatile Hydrocarbons	13.0 (±5)	11.2 (±0.9)	8.6 (±0.9)	6.5 (±0.5)
Aliphatic Hydrocarbons	5.0 (±2.6)	3.6 (±0.9)	2.0 (±0.2)	1.1 (±0.4)
Aromatic Hydrocarbons	7.9 (±3.0)	7.7 (±0.6)	6.6 (±0.6)	5.4 (±0.2)
Dissolved Non-volatile Organics	293 (±16)	409 (±20)	394 (±29)	423 (±11)
Total Organic Load	454 (±137)	458 (±30)	436 (±8)	435 (±14)

TABLE 6. STEPWIDE REDUCTION OF ORGANIC CONTENT IN PROCESS WATER BY THE TREATMENT PROCESS, TRADING BAY, ALASKA, PRODUCTION FACILITY, JANUARY 23, 1980

Organic Composition	Effluents (Concentration in mg C/L) Heater-Treater	Gravity Separator	Gas Flotator	Impound Basin (Final Effluent)
Suspended Petroleum	148	38	33	5
Reduced by (%)		(74.3)	(77.8)	(96.6)
Dissolved Organics	293	409	394	423
Reduced by (%)		(-)	(-)	(-)
Volatile Hydrocarbons	13.1	11.2	8.6	6.5
Reduced by (%)		(14.5)	(34.4)	(47.3)
. Aromatic	7.9	7.7	6.6	5.4
Reduced by (%)		(2.5)	(16.5)	(29.1)
. Aliphatic	5.0	3.6	2.0	1.1
Reduced by (%)		(28.0)	(60.0)	(74.0)

% Reduction = $\frac{(C_o - C_n)}{C_o} \cdot 100$ where C_o is initial concentration in the effluent from the heater-treater and C_n is the concentration in effluents from various process units.

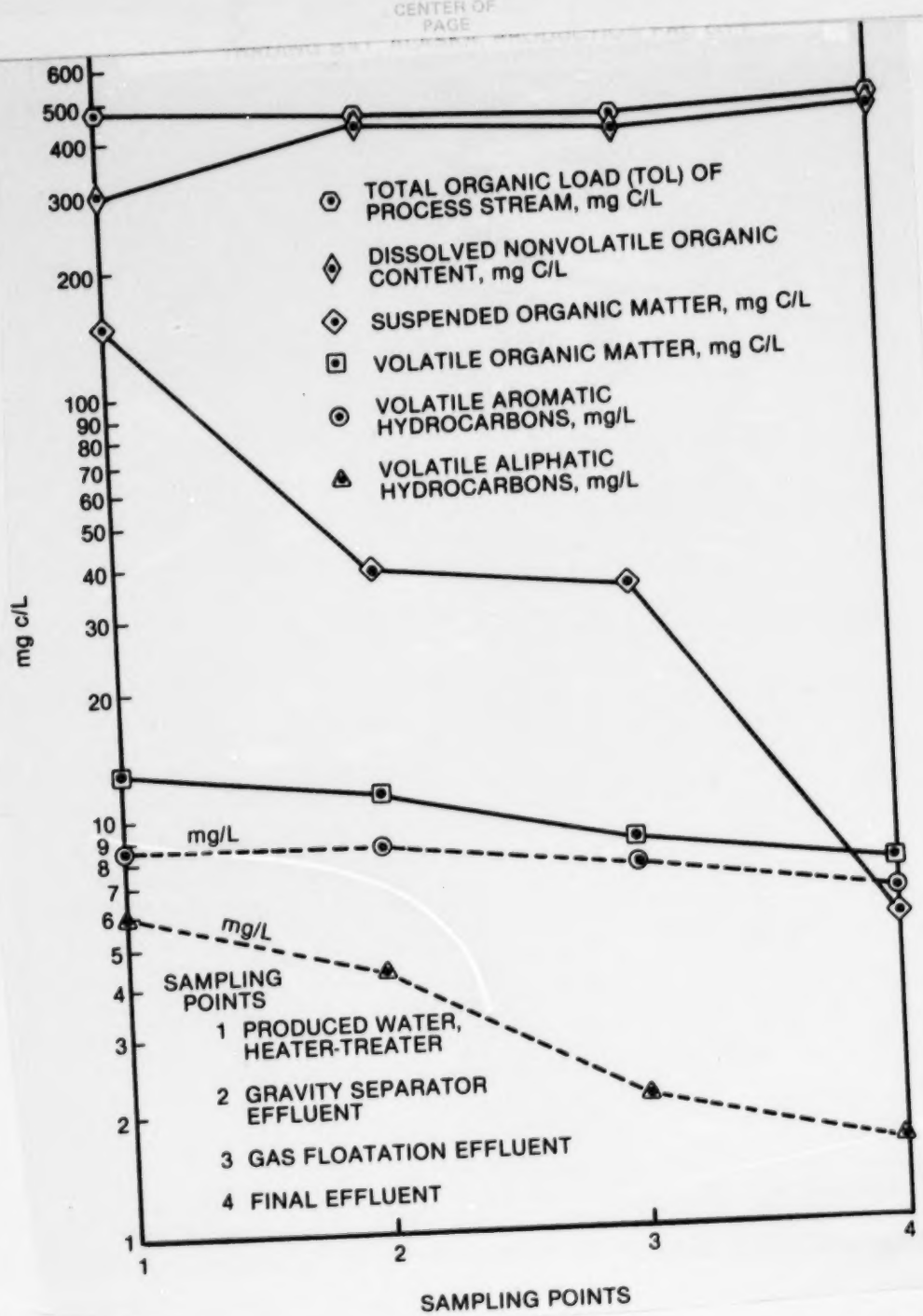

Figure 3. Reduction of organic composition in produced water by a multistage treatment plant, Trading Bay, Alaska, production facility.

Kenai Production Facility

Evaluation of the treatment effectiveness at the Kenai production facility was conducted on 7 August 1980. This facility is located approximately 60 air miles southwest of Anchorage on the southwestern shore of Cook Inlet. Three offshore platforms servicing a number of wells provide gross fluid for onshore processing. Processing includes free water knockout, followed by additional separation of oil from water in heater-treaters. Produced water is treated in skim tanks (gravity separators) followed by dissolved air flotation with addition of flocculating agents.

The retention time of produced water in the treatment plant is approximately 6 hours. The facility processes 21,000 barrels (3339 m^3) of gross fluid a day and typically generates 13,000 barrels (2067 m^3) of oil and 8000 barrels (1272 m^3) of produced water. This facility produces gross fluid with a higher oil content than the two other facilities evaluated in this study.

Sampling and Analysis--

The process stream was sampled at two points: Station 1, effluent from the oil separator, and Station 2, final effluent from the dissolved air flotation unit. Duplicate samples were collected at each station and analyzed for suspended organic matter, dissolved nonvolatile organic matter, and volatile hydrocarbons.

Results--

Station 1, Effluent from Oil Separator. Two samples were collected at this station on August 7, 1980. The results of oily wastewater protocol analysis, which represents material balance for all organic matter present in the sample, are reported in Table 7. The average total organic load in the effluent from the water separator was 544 mg C/L (a range of 445 to 643 mg C/L). Suspended organic matter, composed primarily of free oil, was found to average 190 mg C/L (79 to 301 mg C/L range). Dissolved nonvolatile organic matter was present in an average concentration of 336 mg C/L (a range of 322 to 350 mg C/L). Volatile hydrocarbon fraction averaged 18 mg C/L (a range of 16 to 20 mg C/L). Volatile hydrocarbons were composed of 1.4 mg C/L aliphatic hydrocarbons (8%), and 16.4 mg C/L aromatic hydrocarbons (92%). Aromatic hydrocarbons were composed essentially of benzene, toluene, and xylenes/ethylbenzene in a ratio of approximately 4.3:1.8:1. The effluent from the oil separator was composed of 35% free oil, 62% dissolved nonvolatile matter, and 3% volatile hydrocarbons.

Station 2, Final Effluent. Two samples were collected at this station on August 7, 1980. The results of oily wastewater protocol analysis, which represent material balance for all organic matter present in the sample, are reported in Table 8. The average total organic load in the final effluent was 288 mg C/L (a range of 285 to 291 mg C/L). Free oil was present in a concentration of 14 mg C/L (a range of 13 to 14 mg C/L), while dissolved nonvolatile organic matter was found at 264 mg C/L concentration (a range of 262 to 266 mg C/L). Volatile hydrocarbons were present at approximately the 10 mg C/L level, and consisted of 90% aromatic hydrocarbons. The principal compounds found were benzene, toluene, and xylenes/ethylbenzene in an approximate ratio of 5.7:2.6:1. The final effluent was composed largely of dissolved nonvolatile

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TABLE 7. ORGANIC COMPOSITION OF EFFLUENT FROM OIL SEPARATOR, AUGUST 7, 1980, KENAI PRODUCTION FACILITY

	Concentration (mg C/L)			
	High	Low	Average	%
Total Organic Load	643	445	544	
Suspended Petroleum	301	79	190	35
Dissolved Nonvolatile Organic Matter	350	322	336	62
Volatile Hydrocarbons	19.6	16	17.9	3
Volatile Aliphatic Hydrocarbons	2.1	0.7	1.4	0.3
Volatile Aromatic Hydrocarbons	17.5	15.3	16.5	3.0
Benzene	10.2	9.8	10.0	
Toluene	4.3	4.0	4.2	
Xylenes	3.0	1.5	2.3	

Note: Water temperature was 45°C.

matter (92%). Free oil was at 5%, while volatile hydrocarbons were at 3%.

Discussion--

The reported data (Table 9) reveals that the treatment process reduced concentrations of suspended oil from an average of 190 mg C/L to 14 mg C/L, or approximately 93%. The volatile hydrocarbons were reduced approximately 45%, and the treated effluent contained significant amounts of volatile aromatic hydrocarbons. The BTX (benzene, toluene, and xylenes/ethylbenzene) was present in the effluent at an average concentration level of 9 mg C/L.

Dissolved nonvolatile organic matter was present in the effluent from the oil/water separator at a concentration of 336 mg C/L and at 264 mg C/L in the final treated effluent. It constituted approximately 92% of the total organic load discharged into the receiving environment.

An effort was made to determine the source of the high concentrations of dissolved nonvolatile organic matter in the treated effluent. Discussions with

TABLE 8. ORGANIC COMPOSITION OF FINAL EFFLUENT, AUGUST 7, 1980, KENAI, ALASKA, PRODUCTION FACILITY

	Concentration (mg C/L)			
	High	Low	Average	%
Total Organic Load	291	284	288	
Suspended Petroleum	14	13	14	5
Dissolved Nonvolatile Organic Matter	266	262	264	92
Volatile Hydrocarbons	11.2	8.9	10.1	3
Volatile Aliphatic Hydrocarbons	1.0	0.7	0.9	0.3
Volatile Aromatic Hydrocarbons	10.2	8.2	9.3	3.0
Benzene	5.9	5.4	5.7	
Toluene	2.9	2.3	2.6	
Xylenes	1.4	0.5	1.0	

Note: Water temperature was 43.9°C.

plant operating personnel disclosed that because chemical additives are used at at many points of gross fluid processing, obtaining a sample of produced water that was not treated in some way is very difficult. A possible source of untreated produced water would be at well heads of newer oil wells, which do not require reinjection. Such a sample of untreated gross fluid was obtained from one of the offshore oil wells supplying the Kenai production facility.

The sample consisted of approximately 80% oil and 20% water. Analysis of the aqueous phase revealed that average concentrations of dissolved nonvolatile organics in this sample was equal to 50 mg C/L.

There was apparently a substantial rise in dissolved organic content between the oil well head (50 mg C/L) and the effluent from the oil/water separator (336 mg C/L). The rise could be attributed in part to the addition of chemicals and in part to chemical compositional changes that resulted in the formation of additional water-soluble organic composition.

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TABLE 9. EFFECTIVENESS OF TREATMENT PROCESS, AUGUST 7, 1980, KENAI, ALASKA, PRODUCTION FACILITY

	Average Concentration (mg C/L)		
	Station 1 Water/Oil Separator	Station 2 Final Effluent	% Reduction
Total Organic Load	544	288	47
Suspended Petroleum	190	14	93
Dissolved Nonvolatile Organic Matter	336	264	22
Volatile Hydrocarbons	18	10	45
Volatile Aliphatic Hydrocarbons	1.4	0.9	36
Volatile Aromatic Hydrocarbons	16.5	9.3	44
Benzene	10.0	5.7	43
Toluene	4.2	2.6	38
Xylenes	2.3	1.0	56

Note: Water temperature was 44.5°C.

Offshore (Dillon) Platform, Cook Inlet, Alaska

Evaluation of treatment effectiveness on the Cook Inlet offshore platform was conducted on August 6, 1980. This platform is one of the older ones in Cook Inlet. The gross fluid is processed on the platform, as is the produced water, which is then discharged into Cook Inlet. The platform typically processes 13,000 barrels (2067 m^3) of gross fluid per day, generating 2000 barrels (318 m^3) of oil and 11,000 barrels (1749 m^3) of produced water. Extracted gross fluid contains approximately 85% water. The oil/water separation process and treatment of produced water are very simple, one-step operations. The oil separation process consists of a free water knockout unit (no heater-treaters), and the produced water is treated in one step by a gravity separator.

Sampling and Analysis--

Two sampling points were selected on this platform: Station 1, the effluent from the water knockout unit, and Station 2, final effluent. Triplicate samples were collected at each station and analyzed for suspended oil, dissolved nonvolatile organic matter, and volatile hydrocarbons.

Results--

Station 1, Water Knockout Effluent. Three samples were collected at this

station on August 6, 1980. The results of protocol analysis, which represents material balance for all organic matter present in the sample, are reported in Table 10. The average total organic load of the water knockout effluent was 656 mg C/L, with a standard deviation of 298 mg C/L (an approximate fluctuation of 53%). Suspended organic matter, composed primarily of free oil, was found to be at a 405 mg C/L level, with a standard deviation of 309 mg C/L.

Dissolved nonvolatile organic matter was present in an average concentration of 129 mg C/L, with a standard deviation of 5 mg C/L (a fluctuation of approximately 4%). A low order of fluctuation in dissolved organic content of the process stream observed was consistent with observations at other test sites, indicating a constancy of this fraction of organic load. The concentration level of volatile organic fraction was found to be 31 mg C/L, with a standard deviation of 10 mg C/L (an approximate fluctuation of 32%). Volatile hydrocarbons were composed of 7.8 mg C/L aliphatic hydrocarbons (25%) and 22.7 mg C/L aromatic hydrocarbons (75%). Aromatic hydrocarbons were composed essentially of benzene, toluene, and xylenes/ethylbenzene, in a ratio of approximately 2:1.2:1.

Data reported in Table 10 reveals that the effluent from the water knockout unit was composed of 72% free oil, 23% dissolved nonvolatile organic matter, and 6% volatile hydrocarbons. The lowest value (129 mg C/L) and lowest proportion (23%) of dissolved organic matter in incoming process water was observed at this processing facility. This facility was the simplest in design, involving only one unit process for separating oil from water, and only one unit for treating produced water. There were no heater-treaters in the process.

It appears that the contribution from the processing of gross fluid at this platform was a minimum, and this fact was reflected in low values for dissolved nonvolatile matter observed.

Station 2, Final Effluent. Three samples of gravity separator effluent were collected on August 6, 1980. The results of oily wastewater protocol analysis are reported in Table 11. The total organic load of the gravity separator effluent was 188 mg C/L, with a standard deviation of 8 mg C/L (a fluctuation of approximately 4%), a value considerably lower than that observed in the effluent from the water knockout unit. Suspended organic matter, or free oil, was found to be 36 mg C/L, with a standard deviation of 11 mg C/L (a fluctuation of approximately 30%). The concentration of free oil in effluent from the gravity separators in the onshore facility in Trading Bay (38 mg C/L) was close to the concentration of free oil observed on the offshore platform (36 mg C/L).

Dissolved organic matter was present in a concentration of 141 mg C/L, with a standard deviation of 6.1 mg C/L (a fluctuation of approximately 4%). High reproducibility of dissolved organic content in this case was consistent with all previous observations on the consistency of this fraction in process streams and samples thereof. Volatile hydrocarbons were present at an 11 mg C/L level (standard deviation of 0.4 mg C/L) and were composed of 0.7 mg C/L aliphatic hydrocarbons and 10.2 mg C/L aromatic hydrocarbons. Benzene, toluene, and xylenes/ethylbenzene were the principal hydrocarbons present. Their ratio was 4.9:2.6:1.

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TABLE 10. ORGANIC COMPOSITION OF WATER KNOCKOUT EFFLUENT, AUGUST 6, 1980, COOK INLET OFFSHORE PLATFORM

Component	Concentration (mg C/L) Determinations			Avg	Standard Deviation	%
Total Organic Load	677	790	228	565	298	
Suspended Petroleum	524	638	54	405	309	72
Dissolved Nonvolatile Organic Matter	124	131	133	129	4	23
Volatile Hydorcarbons	29.3	21.7	40.7	30.5	10	5
Volatile Aliphatic Hydrocarbons	10.7	4.7	8.1	7.8	3.0	1
Volatile Aromatic Hydrocarbons	18.6	17.0	32.6	22.7	8.7	4
Benzene	9.4	8.4	15.2	11.0	3.7	
Toluene	5.2	4.6	9.2	6.3	2.5	
Xylenes	4.0	4.0	8.2	5.4	2.4	

Note: Water temperature was 52.2°C.

Data reported in Table 11 reveals that dissolved nonvolatile organics were the largest component of the treated effluent (75%). Free oil contributed 19% to the total organic load of the effluent, while volatile hydrocarbons added 6%.

Discussion--

A summary of compositional data is presented in Table 12. Reported are average values of all parameters measured and their standard deviation. Significant fluctuations in levels of free oil in triplicate samples was observed. The reason for this is nonhomogeneity of oil-water mixtures. It appears that multiple or composite (perhaps 24-hour composites) mode of sampling for free oil is indicated in this type of installation. The dissolved organic content of the process stream as reflected in multiple sampling appears to be far more reproducible and single grab samples in this case should suffice. The volatile hydrocarbon content of process stream influent fluctuates to a significant degre, but is quite reproducible downstream from the gravity separator. Generally speaking, reproducibility of multiple sampling on the offshore platform was very similar to reproducibility of samples obtained during a 5-hour period of sampling at discrete time intervals at the onshore Trading Bay facility.

TABLE 11. ORGANIC COMPOSITION OF FINAL EFFLUENT, AUGUST 6, 1980, COOK INLET OFFSHORE PLATFORM

Component	Concentration (mg C/L) Determinations			Avg	Standard Deviation	%
Total Organic Load	185	197	181	188	8	
Suspended Petroleum	26	48	33	36	11	19
Dissolved Nonvolatile Organic Matter	148	138	137	141	6	75
Volatile Hydrocarbons	10.9	11.4	10.8	10.9	0.5	6
Volatile Aliphatic Hydrocarbons	0.7	0.8	0.7	0.7	0.1	0.4
Volatile Aromatic Hydrocarbons	10.2	10.6	10.1	10.2	0.3	5.4
Benzene	5.8	6.1	5.9	5.9	0.2	
Toluene	3.1	3.2	3.1	3.1	0.1	
Xylenes	1.3	1.3	1.1	1.2	0.1	

Note: Water temperature was 47.2°C.

This similarity suggests that the principal reason for poor reproducibility of free oil measurement might be due to sampling operations and consequently, composite sampling for this parameter is indicated when the process stream or final effluent are sampled. The reproduction of measurements for dissolved organic content including volatile hydrocarbons appears to be good, especially downstream from the gravity separator, and single grab samples might be sufficient for measurements of priority pollutants.

Reduction in concentration of various fractions of organic load of the process stream is reported in Table 12. The suspended oil content was reduced from 405 mg C/L to 36 mg C/L (approximately 91%). The volatile aromatic hydrocarbons were present in the final effluent at an 11 mg/L concentration, the highest level observed in this study. The dissolved nonvolatile organic compounds were present in significantly high levels, both in the effluent from the water knockout unit (129 mg C/L) and in the final effluent (141 mg C/L). Such compounds constitute approximately 75% of the total organic load in the effluent.

TABLE 12. ORGANIC COMPOSITION OF PROCESS STREAM, AUGUST 6, 1980, COOK INLET OFFSHORE PLATFORM

	Station 1		Station 2		
	Water Knockout Average Conc.	Standard Deviation	Final Effluent Average Conc.	Standard Deviation	% Reduction
Water Temperature, ^{o}C	52.2		47.2		
Total Organic Load	565	±298	188	± 8	67
Suspended Petroleum	405	±309	36	±11	91
Dissolved Nonvolatile Organic Matter	129	± 4	141	± 6	--
Volatile Hydrocarbons	31	± 10	11	±0.5	65
Volatile Aliphatic Hydrocarbons	7.8	± 3	0.7	±0.1	91
Volatile Aromatic Hydrocarbons	22.7	±8.7	10.2	±0.3	55
Benzene	11.0	±3.7	5.9	±0.2	46
Toluene	6.3	±2.5	3.1	±0.1	51
Xylenes	5.4	±2.4	1.2	±0.1	77

Note: All values are reported in mg C/L.

GULF OF MEXICO

Characterization of the effluent quality from seven offshore platforms was carried out in the Gulf of Mexico. Two different types of analyses were performed. Using oily wastewater protocol analysis (1, 5), the total organic load of the samples was characterized including free oil content, dissolved nonvolatile organics, and volatile hydrocarbons. Using EPA priority pollutants analysis, determinations were made of purgeable, acid-neutral, base-neutral, pesticides, and metal priority pollutants.

Sets of samples were collected from each platform for oily wastewater protocol analysis. These samples were acidified (after arrival at Newbury Park, California) to pH 2 with hydrochloric acid and then analyzed. A set of samples for priority pollutant analysis was collected by Rockwell and analyzed by EPA Effluent Guidelines Division contract laboratories according to sampling and analytical instructions as described in the Federal Register (4).

Offshore Platforms

The seven offshore production platforms selected for this study represented a range of the variables found off the Louisiana coast (2). All examined sites treated produced water offshore. While specifics of hardware design and the nature and quantity of chemicals used differed from platform to platform, the treatment principles were the same: primary treatment by gravity separation, followed by secondary treatment by gas flotation.

Platform 1 (BM 2C)

Samples on platform 1 were collected for protocol analysis on March 7, 1980, and for priority pollutants on March 13, 1980. The estimated daily production of the 23 wells that were supplying gross fluid for processing was 16,483 barrels of gross fluid (2621 m^3/d) and 13,085 MCFD (370,530 standard m^3/d) of natural gas. Oil production corresponded to 11,957 barrels per day (1901 m^3/d) and water was produced at a rate of 4526 barrels per day (720 m^3/day). Water constituted approximately 22% of the gross fluid.

The produced water treatment on this platform consisted of two units: a corrugated plate interceptor (CPI) unit and a gas flotation (Wemco) unit. In this system the primary produced water from a low-pressure separator flows to the CPI (manufactured by Monarch Separators, Inc.) for gravity separation and then into the Wemco gas flotator (mechanical eductor) for gas flotation. The effluent from the gas flotator is discharged overboard.

Two chemicals are added to the process stream. Tretolite RP-34 (a demulsifier) is added at the low-pressure separator inlet manifold at a rate of 15 dm^3/day. A flotation aid (Tretolite FR-87) is added at the flotation unit inlet at a rate of 17 dm^3/day. Based on an approximate 720 m^3/day discharge, it can be calculated that added chemicals correspond to approximately 44 ppm concentration in the process stream.

Platform 2 (SS 107)

Samples on platform 2 were collected for oily wastewater protocol analysis on March 10, 1980. No samples were collected for priority pollutants on this platform. The estimated daily production of five wells at this platform was 610 bpd (97 m^3/d) of oil, 3979 bpd (633 m^3/d) of water, and 470 MCFD (13,300 standard m^3/d) of natural gas. Total gross fluid output was 4589 bpd (730 m^3/d) with water contributing 87% to the flow.

The treatment of produced water at this platform consists of two units: a gravity separator and a gas flotator. In this system the fluids from the low-pressure separator flow to the oil treater, which is a dual-purpose unit providing for the gravity separation of water from oil, producing processed oil. It also provides for gravity separation of oil from water to prepare the water for treatment by flotation. The flotation unit is a proprietary four-cell assembly with mechanical gas eduction. The effluent from the gas flotator is discharged.

Four chemicals are added to the process stream: methanol was added at the lift gas point at a rate of 8 dm^3/d; Tretolite RN3003 (a demulsifier) is added at the well manifold at a rate of 8.6 dm^3/d; Tretolite SP175 (a scale inhibitor) is added at the low-pressure separator outlet at 7.3 dm^3/d; and a flotation aid, Tretolite FR98D, is added upstream of the flotation unit at an average rate of 10 dm^3/d. Based on an average measured 730 m^3/d discharge, it can be calculated that added chemicals constitute 47 ppm in the process stream.

Platform 3 (ST 131)

Samples on this platform were collected for oily wastewater protocol analysis on March 21, 1980, and for priority pollutants on March 19, 1980. The estimated production of this platform was 1853 bpd (295 m^3/d) of oil and 870 bpd (138 m^3/d) of water, for a total of 2723 bpd (433 m^3/d) of gross fluid. Calculated water content is 32%. Additionally, 7623 MCFD (215,700 standard m^3/d) of natural gas is produced.

The treatment process for produced water at this platform consists of two steps: gravity separation in a gun-barrel unit, and gas flotator with mechanical gas dispersion. The effluent from the gas flotator is discharged.

Two chemicals were added to the process stream: Tretolite RP-101 (a demulsifier) was added at the low-pressure well manifold at a rate of 3.8 dm^3/d, and Tretolite FR-81 (a flotation aid) was added at the flotation unit inlet at 14 dm^3/d. From the discharge rate it can be calculated that 129 ppm of chemicals are added to the process stream.

Platform 4 (SS 198G)

Samples on this platform were collected for oily wastewater protocol analysis on March 24, 1980, and for priority pollutant analysis on March 25, 1980. The average daily production for this platform was 593 bpd (94 m^3/d) of oil and 195 bpd (31 m^3/d) of water, for a total of 788 bpd (125 m^3/d) of gross

fluid. The water cut was approximately 25%. Additionally, 14,320 MCFD (405,000 standard m^3/d) of natural gas is produced.

The produced water is treated on the platform in three steps: gravity separation by corrugated plate interception (CPI) and in two flotation units operating in series. The CPI unit is a gravity separator of proprietary design supplied by Monarch Separators, Inc. The first flotation unit is a Tridair (a proprietary three-cell dispersed gas flotator with hydraulic gas eduction), the second flotator was a one-cell proprietary device manufactured by Monosep. The gas for the flotator was educted hydraulically.

Three chemicals were added to the process stream. Tretolite RP2327 (a demulsifier) was added at a rate of 13.2 dm^3/d, and Tretolite SP246 (a scale inhibitor) was added at a rate of 1.7 dm^3/d at the well manifold. A flotation aid, Tretolite FR88, was added upstream of the flotation unit at an average rate of 1.8 dm^3/d. This addition of chemicals relative to treated effluent discharge amounted to a concentration of 539 ppm.

Platform 5 (EI 18CF)

Samples of treated effluent were collected for material balance on April 2, 1980, and for priority pollutants on April 8, 1980. The average daily production on this platform is estimated at 18,893 bpd (3004 m^3/d) of gross fluid which contained approximately 90% water. Oil was produced at a rate of 1856 bpd (295 m^3/d) and water at a rate of 17,037 bpd (2709 m^3/d). Additionally, 38,089 MCFD (1,078,000 standard m^3/d) of natural gas was produced.

The treatment process on this platform was a two-step operation. Produced water from the oil treater is directed into a skim tank, where residual oil is separated by gravity. The effluent from the skim tanks enters the dissolved gas flotator where additional separation takes place. The effluent from the flotation unit is discharged.

Methanol was added at the high-pressure well heads to prevent hydrate formation at a rate of 115 dm^3/d. No other chemicals were added to the process. The addition of methanol corresponded to an approximate 42 ppm concentration contribution relative to the discharge rate.

Platform 6 (BDC CF5)

Samples for oily wastewater protocol analysis were taken at this platform on April 4, 1980. Samples for priority pollutant analysis were taken on April 8, 1980. The estimated daily production for this platform was 13,026 bpd (2070 m^3/d) of gross fluid that contained approximately 91% water. Oil was produced at a rate of 1131 bpd (180 m^3/d) and water at a rate of 11,895 bpd (1890 m^3/d). Additionally, 5145 MCFD (145,000 standard m^3/d) of natural gas was produced.

The oil was separated from water in two heater-treaters connected in parallel. The effluent from the heater-treaters was introduced into two gravity separators, which were also connected in parallel. The effluent from the two gravity separators was recombined and introduced into a gas flotation unit (Monosep) with hydraulic gas dispersion.

Three chemicals were added to the process stream. A scale inhibitor, Tretolite WF-123, was added to the manifold ahead of the low-pressure separators at a rate of 0.95 dm^3/d. A demulsifier, Tretolite BR-4050, was added at a rate of 5.3 dm^3/d at the same manifold. A flotation aid, Tretolite JW8206, was added at an average rate of 9.4 dm^3/d at the inlet to the flotation unit. This addition of chemicals contributed approximately 8 ppm relative to the discharge flow.

Platform 7 (SM 130B)

Samples for priority pollutant analysis were collected at this platform on April 17, 1980. No oily wastewater analyses were performed at this site. The average daily production of gross fluid at this site was 21,136 bpd (3361 m^3/d). Oil was produced at a rate of 17,170 bpd (2730 m^3/d) and water at a rate of 3966 bpd (631 m^3/d). The calculated water cut was 19%. Additionally, 8377 MCFD (237,200 standard m^3/d) of natural gas was produced.

The treatment process included gravity separation by two corrugated plate interceptors (CPI) connected in parallel, followed by secondary treatment in a flotation unit with mechanical gas eduction.

A foam inhibitor (Dow Corning 200) was added to produced fluids at the manifold ahead of the low-pressure separator. The inhibitor was diluted with diesel to a concentration of 15%. The diluted mixture was fed at a concentration of 3.5 ppm.

Organic Material Balance Results

Organic material balance in the effluents from offshore platforms in the Gulf of Mexico is reported in Table 13. The total organic load of treated effluents ranged between 68 and 661 mg C/L, with an average value of 404 mg C/L. Dissolved nonvolatile organic matter constituted the great bulk of organic matter in the discharge. The concentration of this fraction ranged between 57 and 624 mg C/L, with an average of 376 mg C/L. On the average, this fraction constituted 93% of all organic matter discharged from platforms. Similarly high nonvolatile dissolved organic content was observed in treated produced water in Cook Inlet fields. On the average, 88% of the organic matter discharged there was composed of dissolved nonvolatile organics.

Concentrations of suspended organics (free oil) ranged between 9 and 46 mg C/L, averaging 26 mg C/L. This range was not unlike the one observed in Cook Inlet production fields, where the range of suspended organics was from 5 to 36 mg C/L.

With the exception of platform 5, the concentration of volatile hydrocarbons was low, and fluctuated in a narrow range of 0.9 to 2.2 mg C/L. This fraction constituted only 0.5% of the total organic load in the discharged water and was considerably lower than that observed in Cook Inlet platform effluent. The range for volatile hydrocarbons in samples from Cook Inlet was 7 to 11 mg C/L.

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TABLE 13. ORGANIC MATERIAL BALANCE IN EFFLUENT FROM OFFSHORE PLATFORMS IN GULF OF MEXICO

Date, 1980	Platform	Concentration, mg C/L			
		Volatile Aromatic Hydrocarbons	Suspended Organics (free oil)	Dissolved Nonvolatile Organics	Total Organic Load
3/7	1	1.7	35	495	532
3/10	2	3.1	21	561	584
3/21	3	3.1	10	382	394
3/24	4	0.9	36	624	661
4/2	5	5.3	46	136	188
4/4	6	2.2	9	57	68
Average		2.1	26	376	404
Coefficient of Variance		0.68	0.46	0.39	0.37

It must be noted that hydrochloric acid was added to Gulf of Mexico produced water only after samples were received in Newbury Park, California, and considerable time was spent in transit between the Gulf Coast and Valdez, Alaska, where the samples were analyzed. The possibility of some aromatic hydrocarbon decomposition in unpreserved samples during shipment cannot be ruled out.

Benzene, toluene, xylenes/ethylbenzene constituted the principal organic compounds present in the effluent. On the average, 1.1 mg/L of benzene, 0.8 mg/L of toluene, and 0.3 mg/L of xylenes/ethylbenzene were present in the effuent from offshore platforms in the Gulf of Mexico and, for comparison, in Cook Inlet (Table 14).

Because dissolved nonvolatile organic matter constituted the bulk (93%) of all organic matter discharged from offshore platforms in the Gulf of Mexico, its possible source is of some interest. It is possible that part of it may originate in brine, part is formed during the processing of gross fluids, and part derives from chemicals used in processing and treatment of produced water.

Chemicals added to the process stream include demulsifiers, corrosion inhibitors, and flotation aids. Methanol is sometimes added to prevent hydrate formation at high-pressure well heads. An estimate (in ppm) of additives added to the processing stream at each platform studied was made and is reported in Table 15, as is the contribution to the Total Organic Load (TOL). The values ranged from 8 to 539 ppm. Low concentrations for chemical addition were normally observed at platforms discharging high volumes of brine, i.e., water discharge from platform 6 was 1890 m^3/d and an equivalent of 8 ppm of chemical additives were in the process stream. On the other hand, platform 4 was discharging only 31 m^3/d of produced water and chemical additions to the process stream amounted to 539 ppm. The weighted (by volume of discharge) average addition of chemicals to the process stream for the platforms studied was 37 ppm. This value can account for approximately 10% of the dissolved nonvolatile organic fraction, found in discharges from offshore platforms.

From this it may be concluded that the bulk of dissolved nonvolatile organics originate either in brine or are formed during the processing of gross fluid. It is unknown at this time which source (original brine composition, or effects of processing) contributes to what degree to the observed high level of dissolved organic content. Completed studies indicate only that such organic matter is universally present in all treated effluent from offshore oil extraction operations, and constitutes approximately 90% of all organic matter discharged. Neither source nor exact chemical nature of this fraction is known at this time.

Priority Pollutants Analysis

After receiving the results of the EPA Effluent Guidelines Division contract laboratories' analyses, four groups of organic priority pollutants were examined in effluents from six offshore platforms in the Gulf of Mexico: purgeable, base-neutral, acid-neutral, and pesticides.

TABLE 14. VOLATILE AROMATIC HYDROCARBONS IN TREATED EFFLUENTS FROM OFFSHORE PLATFORMS IN THE GULF OF MEXICO AND COOK INLET

Date, 1980	Platform	Concentration in mg/L Benzene	Toluene	Xylenes/ Ethylbenzene	Total
Gulf of Mexico					
3/7	1	0.9	0.7	0.3	1.9
3/10	2	0.5	0.6	0.3	1.4
3/21	3	0.8	0.4	0.2	1.4
3/24	4	0.4	0.4	0.2	1.0
4/2	5	2.4	2.1	0.3	5.8
4/4	6	1.4	0.7	0.3	2.4
Average and Standard Deviation		1.1 ±0.6	0.8 ±0.6	0.3 ±0.05	2.2 ±1.8
Cook Inlet					
1/22	Trading Bay	3.7	1.9	0.5	6.1
7/7	Kenai	6.3	2.9	0.9	10.1
7/6	Offshore Cook Inlet	6.5	3.4	1.3	11.2
Average and Standard Deviation		5.5 ±1.6	2.7 ±0.8	0.9 ±0.4	9.1 ±2.7

Purgeables. Samples were analyzed for 31 purgeable priority pollutants. Only benzene, toluene, and ethylbenzene were found in treated effluents. They were the only three priority pollutants consistently present in samples of produced water from offshore platforms in the Gulf of Mexico (Table 16). Benzene concentration as determined by the priority pollutant analysis ranged between 170 µg/L (0.17 mg/L) and 1900 µg/L (1.9 mg/L), averaging 0.9 mg/L. The range for benzene as determined by oily wastewater protocol analysis was 0.4 mg/L to 2.4 mg/L, with an average of 1.1 mg/L (Table 14).

TABLE 15. ESTIMATES OF CHEMICALS ADDED TO THE PROCESS STREAM AND DISSOLVED ORGANIC CONTENT OF TREATED EFFLUENT

Date, 1980	Platform	Production Oil m^3/d	Production Water m^3/d	Concentration (ppm) Dissolved Nonvolatile Organics	Concentration (ppm) Added Chemicals Estimated	Concentration (ppm) % Added Chemicals in TOL
3/7	1	1901	720	495	44	9
3/10	2	97	633	561	47	8
3/21	3	295	138	382	129	34
3/24	4	94	31	624	539	86
4/2	5	295	2709	136	42	31
4/4	6	180	1895	57	8	14
Average and Standard Deviation				376 ±232	135 ±202	

The toluene concentration in the treated effluent ranged between 770 µg/L (0.77 mg/L) to 3300 µg/L (3.3 mg/L), averaging 2.074 mg/L. This value was generally higher than that determined by oily wastewater protocol, where the average value for toluene was found to be 0.8 mg/L and the range 0.7 to 2.1.

Ethylbenzene was found in the range from 42 µg/L to 200 µg/L. This value cannot be compared with material balance protocol analysis because ethylbenzene and xylenes are not resolved in the latter.

One sample (Platform 6) was found to contain rather large quantities of methylene chloride (35,000 µg/L) and carbon tetrachloride (140 µg/L). There was no record of use of such chemicals on Platform 6, and analysis of the influent (untreated brine) disclosed an absence of both methylene chloride and carbon tetrachloride in incoming produced water. Because those chemicals are common laboratory solvents and were found to be absent from all other samples analyzed, they might be due to laboratory contamination of this specific sample. Because of possible sample contamination, the data from Platform 6 is not considered in this discussion.

Base-Neutrals. Naphthalene was found in effluents from three platforms (out of six analyzed). (See Table 17.) Its concentration ranged between 12 µg/L to 44 µg/L. Anthracene/phenanthrene was found in effluent from one platform in a concentration of 15 µg/L. None of the other base-neutral priority pollutants was found in any of the samples analyzed.

TABLE 16. PURGEABLE PRIORITY POLLUTANTS IN OFFSHORE PRODUCED WATER, GULF OF MEXICO

Platform Number:	1	3	4	5	7		
Date of Sampling:	3/13/80	3/19/80	3/25/80	4/8/80	4/17/80	Average	Coefficient of Variance
	Concentration, micrograms/liter						
Treated Effluent							
Benzene	880	170	790	1900	440	836	.788
Toluene	1500	3100	1700	3300	770	2074	.524
Ethylbenzene	94	118	51	200	42	101	.628

TABLE 17. BASE-NEUTRAL PRIORITY POLLUTANTS IN OFFSHORE PRODUCED WATER, GULF OF MEXICO

Platform:	1	3	4	5	7
Date of Sampling:	3/13/80	3/19/80	3/25/80	4/8/80	4/17/80
	Concentration in Micrograms/Liter				
Treated Effluent					
Naphthalene	24	12	ND	44	ND
Anthracene/ phenanthrene	ND	ND	ND	ND	15

Note: ND means not detected at the 10-microgram/liter level.

Acid-Neutrals. Only phenol was found in treated effluent from all platforms studied, as shown in Table 18. Its concentration ranged between 18 and 840 µg/L, with an average value of 486 µg/L. None of the other acid-neutral priority pollutants were found.

Pesticides. No pesticides were found in any of the analyzed effluent.

Metals

Treated effluent from five offshore platforms in the Gulf of Mexico were examined for 13 metal priority pollutants: antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn).

Chromium and lead were found in the effluent from each and every platform examined (see Table 19). Lead was found in a range of 160 to 915 µg/L, averaging 597 µg/L; chromium in a range of 59 to 390 µg/L, averaging 260 µg/L.

Nickel and zinc were found in effluents from four platforms (out of five reported). Nickel ranged in concentration from 68 to 1674 µg/L, while zinc was present in a concentration range of less than 25 to 640 µg/L.

Copper, silver, cadmium, and beryllium were found in effluents from three platforms (platforms 4, 5, and 7). Copper was present in a concentration range of less than 25 to 137 µg/L; and silver in a concentration range of less than 1 to 152 µg/L. Cadmium was present in a concentration range of less than 25 to 56 µg/L, and the concentration range for beryllium was less than 1 to 4 µg/L. Concentrations of antimony, arsenic, mercury, selenium, and thallium were generally below the limit of detection for the methods used.

TABLE 18. ACID-NEUTRAL PRIORITY POLLUTANTS IN OFFSHORE PRODUCED WATER, GULF OF MEXICO

Platform:	1	3	4	5	7		
Date of Sampling:	3/13/80	3/19/80	3/25/80	4/8/80	4/17/80		
	Concentrations in Micrograms/Liter					Average	Coefficient of Variance
Treated Effluent							
Phenol	800	840	620	150	18	486	0.779

TABLE 19. METAL PRIORITY POLLUTANTS IN OFFSHORE PRODUCED WATER, GULF OF MEXICO

Treated Effluent from Platform #	Date Sampled	Sb[1]	As[1]	Be[2]	Cd[2]	Cr[2]	Cu[2]	Pb[2]	Hg[1]	Ni[2]	Se[1]	Ag[1]	Tl[1]	Zn[2]
		Concentration in Micrograms/Liter												
1	3/13/80	<10	<25	< 1	<25	59	<25	160	0.4	68	<25	< 1	<100	<25
3	3/19/80	<25	<50	< 5	<25	220	<50	420	<0.3	<250	<100	< 2	<100	640
4	3/25/80	< 5	< 5	2	50	327	100	779	< 1	1395	< 5	108	<55	239
5	4/8/80	< 5	< 5	2	39	303	137	709	< 1	1674	< 5	152	<50	190
7	4/17/80	< 5	< 5	4	56	390	137	915	< 1	1644	< 5	72	<50	333
Average						260		597						

1 - Flameless atomic absorption spectrometry.

2 - Plasma emission spectrometry.

The generated data indicates that significant amounts of metal priority pollutants are discharged from offshore oil extraction platforms. Four metals (lead, chromium, nickel, and zinc) are the most widely distributed inorganic priority pollutants in treated effluent and, together with four organic priority pollutants (benzene, toluene, ethylbenzene, and phenol), constitute the principal contribution of toxicants discharged from offshore oil-producing platforms.

DISSOLVED AND SUSPENDED OIL

The organic composition of treated and untreated produced water (brine) is complex. The produced water contains many types of dissolved organic compounds in addition to suspended or free oil (composed largely of higher aliphatic and aromatic hydrocarbons and other water-soluble components of crude oil). Some dissolved organics originate in the crude oil being extracted (e.g., benzene, toluene, xylenes, ethylbenzene, phenol, plus additional higher molecular weight water-soluble compounds such as esters, carboxylic acids, ketones, pyridines, quinolines, carbozoles, and others). Additional sources of dissolved organic matter in process water are the proprietary demulsifiers, defoamers, and flocculation aids used to facilitate treatment.

Compounds formed during the processing of gross fluid are an additional and (at this time) largely unexplored source of dissolved organics. Oxidation of some compounds of petroleum is believed to be an important source of dissolved organic contribution to the process stream. Studies carried out in offshore fields in Cook Inlet, Alaska, and the Gulf of Mexico have disclosed that dissolved organic compounds are present in large quantities at all produced water processing steps and constitute up to 90% of the total organic load in the treated effluent.

The brine treatment technology is designed to remove suspended organic matter, or "free oil," from the produced water. The oil/water separation is physical in nature and takes advantage of the relative immiscibility and the density differential of oil and water. Separation is achieved by gravity and gas or air flotation. State-of-the-art methods for the physical treatment of oily wastewaters are not designed for removal of petroleum-derived dissolved organics, nor are they capable of such removal.

In order to determine concentration levels of free or treatable oil in produced water, modifications of standard methods for analysis of oil and grease are practiced by industry. The object of such modified determinations is to establish the quantity of free oil considered to be treatable by the state-of-the-art technology, and to rate performance characteristics of the treatment process in terms of removal of treatable (free) oil (rather than in terms of total oil and grease as determined by liquid/liquid extraction techniques, followed by gravimetric or IR spectrometric quantification). It must be mentioned that such methods are used in-house by the oil companies, and are not currently used in setting standards for oil discharges.

The most commonly used methods for determination of free oil are (1) silica gel adsorption analysis, (2) filtered brine method, (3) equilibration, and (4) IR scan (2). All such methods are somewhat empirical in nature and are

greatly influenced by the specific chemical composition of a given source of produced water.

A limited comparison study of two modified methods (silica gel adsorption and filtered brine) were carried out on brine samples collected at Trading Bay, Alaska, production facilities. The differentiation between free and dissolved oil in silica gel adsorption methods is accomplished in the following manner. Oil and grease analysis is performed on Freon TF extract in a routine manner by IR means. Then 3 grams of silica gel are added to the Freon TF extract (100 ml) and the resulting suspension is agitated for 10 minutes using a magnetic stirrer. After the silica gel is settled, the Freon TF extract is reanalyzed for oil and grease. In this procedure an assumption is made that water-soluble petroleum compounds, being of greater polarity than pure hydrocarbons, are selectively adsorbed by the silica gel and consequently removed from solution. The modified method provides a value for free oil, while the differential between standard oil and grease analysis and silica gel modification of the method produces the value of the dissolved oil.

In the filtered brine method, water samples are filtered through a Whatman No. 40 filter prior to extraction into Freon TF and analysis for oil and grease. In this method, dissolved oil is determined directly by extraction of organics from filtered brine into Freon TF, and then analyzing the Freon TF solution for oil and grease by either gravimetric or IR spectrometric procedure. The quantity of free or suspended oil is determined indirectly as a differential between the values obtained by standard oil and grease analysis and the filtered brine method.

Samples of produced water were collected at Station 1 (effluent from heater-treaters), Station 2 (effluent from gravity separator), Station 3 (effluent from gas flotator), and Station 4 (final treated effluent) (Figure 2), on January 23, 1980 at the Trading Bay production facility, Cook Inlet, Alaska. All samples were approximately 1 liter in size. Brine filtration was performed on-site immediately after sample collection. All samples were preserved by acidification to pH 2 and extracted into Freon TF within 2 days of collection.

Results of the analyses are presented in Table 20. In analyzing this data, dissolved oil content should not be confused with dissolved nonvolatile organic matter determined by the TOC method on 0.45-micron filtrate. The TOC value reflects all dissolved organic matter present in the sample, while the dissolved oil value reflects only those organic compounds that are extractable into Freon TF. Many of the dissolved organic compounds present in produced water are not extractable into Freon TF, and consequently dissolved oil values are usually considerably lower than dissolved TOC values.

All analyzed samples contained dissolved oil as defined by silica gel adsorption and filtered brine tests. Generally, the filtered brine method produced higher values for dissolved oil and consequently lower values for free oil than the silica gel adsorption method. Dissolved oil content as determined by the brine filtration method was consistently higher (by 11% to 15%) than similar values obtained by the silica gel adsorption method. Since both methods of analysis are somewhat empirical, no great significance can be ascribed to this fact. It is believed, however, that the silica gel adsorption

TABLE 20. ANALYSIS FOR DISSOLVED AND FREE OIL, TRADING BAY PRODUCTION FACILITY, COOK INLET, ALASKA*, JANUARY 23, 1980 (mg oil/liter)

Effluent Source:	Station 1	Station 2	Station 3	Station 4
Time of Sampling:	1310	1141	1090	1015
	Effluent, Heater-Treater	Effluent, Gravity Separator	Effluent, Gas Flotator	Final Effluent
Slicia Gel Adsorption Method:				
Total Oil	68.1	54.6	18.9	14.2
Free Oil	54.9	42.7	11.8	7.9
Dissolved Oil	13.2	11.9	6.6	6.3
Filtered Brine Method:				
Total Oil	68.1	54.6	18.4	14.2
Free Oil	48.5	38.1	9.8	6.7
Dissolved Oil	19.6	16.5	8.8	7.5

* Single sets of samples collected at indicated times were used for analysis.

method provides a good indication of aliphatic hydrocarbon content of the oily water sample when quantification is performed by IR spectroscopic means.

It was found that dissolved oil fraction as determined by the silica gel adsorption method constituted approximately 20% of the total oil in the effluent from the heater-treater and gravity separator. The same fraction contributed 30% to the total oil in the effluent from the gas flotator and 40% in the final treated effluent. This trend appeared to be consistent with the principles of treatment involved, that is, more efficient removal of nonpolar (and consequently nonwater-soluble) petroleum, with a resulting shift to predominance of dissolved oil in the final treated effluent. Looking at the data in another way, it appears that the treatment process, while removing 86% of the free oil, removes only 48% of the dissolved oil.

Both silica gel adsorption and filtered brine analytical data suggest that treated effluent contains on an average 40% to 50% dissolved oil.

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